TETRAMETHYL LEAD (as Pb) 2534

$Pb(CH_3)_4$ MW: 267.34 CAS: 75-74-1 RTECS: TP4725000

METHOD: 2534, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.075 mg/m^3 (as Pb; skin)
NIOSH: 0.075 mg/m^3 (as Pb; skin)
ACGIH: 0.15 mg/m^3 (as Pb; skin)
(1 ppm = 8.47 mg/m^3 as Pb)

PROPERTIES: liquid; d 1.995 g/mL @ 20 °C; BP 110 °C; MP -27.5 °C; VP 2.9 kPa (22 mm Hg; 245 g/m^3 as Pb) @ 20 °C; lower explosive limit 1.8% v/v in air

SYNONYMS: TML; lead tetramethyl; tetra methyl plumbane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2 resin, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 15 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 98% recovered after 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.04 to 0.18 mg/m^3 (as Pb) (24-L samples) [1]

BIAS: - 0.27%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.112

ACCURACY: ± 22.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOTOIONIZATION DETECTOR

ANALYTE: tetramethyl lead

DESORPTION: 2 mL pentane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 185 °C
-MANIFOLD: 200 °C
-PID: 210 °C
-COLUMN: 75 °C

CARRIER GAS: N_2, 17 mL/min

COLUMN: 6 m x 3-mm OD stainless steel packed with 10% Carbowax 20M on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solution of tetramethyl lead in pentane

RANGE: 1 to 10 µg (as Pb) per sample

ESTIMATED LOD: 0.4 µg (as Pb) per sample [2]

PRECISION ($\hat{S}_r$): 0.0763 @ 0.9 to 3.6 µg (as Pb) per sample [1]

APPLICABILITY: The working range is 0.04 to 0.4 mg/m^3 (as Pb) for a 24-L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises Method S384 [2].

REAGENTS:

1. Pentane (reagent grade).
2. Tetramethyl lead.*
3. Calibration stock solution, 0.4 mg/mL (as Pb). Dissolve 5.16 mg tetramethyl lead (ca. 2.6 µL) in pentane to make 10 mL solution. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD and 6-mm ID, with plastic caps, containing two sections of 20/50 mesh XAD-2 resin (front = 400 mg, back = 200 mg), separated and contained by silylated glass wool plugs. Pressure drop <3.4 kPa @ 1 L/min airflow. Tubes are commercially available (SKC, Inc. ST226-30-06).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with photoionization detector, integrator, and column (page 2534-1).
4. Vials, 4-mL, glass, and PTFE-lined caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-µL, readable to 0.1 µL.
7. Pipets, 1- and 2-mL.

SPECIAL PRECAUTIONS: Tetramethyl lead is extremely poisonous with delayed symptoms [3]. Acute or chronic poisoning may occur if inhaled or absorbed through skin.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 15 to 100 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL pentane to each vial containing 400 mg sorbent, and 1.0 mL pentane to each vial containing 200 mg sorbent. Cap each vial.
   NOTE: A suitable internal standard (e.g., 0.1% v/v nonane) may be added to samples and blanks at this step [1].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to pentane in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain tetramethyl lead concentrations in the range 0.2 to 5 µg/mL (as Pb).
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph [peak area or peak height vs. µg tetramethyl lead (as Pb)].
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (2 to 20 µL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. µg tetramethyl lead (as Pb) recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2534-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Under these conditions, t_r = 6 min for tetramethyl lead.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with pentane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of tetramethyl lead (as Pb) found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of tetramethyl lead (as Pb) in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S384 was issued on April 15, 1977 [2], and validated with generated atmospheres [1,3]. Average recovery was 97.4% ± 6.5% (18 samples) in the range 0.04 to 0.18 mg/m^3 for 24-L samples. No breakthrough occurred after sampling for 240 min at 0.2 L/min from an atmosphere containing 0.312 mg/m^3 tetramethyl lead (as Pb) at 82% RH. Desorption efficiency for eighteen spiked samples in the range 0.89 to 3.6 µg per sample averaged 0.84 with $\bar{S}_r$ = 0.091. Sample migration between front and back sorbent sections was found to be negligible after storage for 10 days at room temperature.

REFERENCES:

[1] A. D. Little, Inc. Backup Data Report S384 prepared under NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB-275-834 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S384, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

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